J. Chem. Thermodynamics 91 (2015) 204–210

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Modified solution calorimetry approach for determination of vaporization and sublimation enthalpies of branched-chain aliphatic and alkyl aromatic compounds at $T = 298.15$ K

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ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form 24 July 2015
Accepted 25 July 2015
Available online 1 August 2015

Keywords:
Solution calorimetry
Enthalpy of solvation
Molar refraction
Enthalpy of sublimation
Enthalpy of vaporization
Alkyl aromatics

ABSTRACT

The enthalpies of solution, solvation and vaporization/sublimation are interrelated values combined in the simplest thermodynamic circle. Hence, experimental determination of vaporization/sublimation enthalpy can be substituted by experimentally simpler determination of solution enthalpy when solvation enthalpy is known. Previously it was found that solvation enthalpies of a wide range of unbranched aliphatic and aromatic solutes in saturated hydrocarbons are in good linear correlation with their molar refraction values. This allows to estimate the vaporization/sublimation enthalpy of any unbranched organic compound from its solution enthalpy in saturated hydrocarbon and molar refraction. In the present work this approach was modified for determination of vaporization/sublimation enthalpy of branched-chain alkyl aromatic and aliphatic compounds. Group contributions to the enthalpy of solvation due to the branching of carbon chain were evaluated. Enthalpies of solution at infinite dilution of 18 branched-chain aliphatic and alkyl aromatic compounds were measured at $T = 298.15$ K. Vaporization/sublimation enthalpies for 35 branched aliphatic and alkyl aromatic compounds were determined by using modified solution calorimetry approach. These values are in good agreement with available literature data on vaporization/sublimation enthalpies obtained by conventional methods.

1. Introduction

The enthalpies of "liquid–gas" and "solid–gas" phase transitions are fundamental characteristics of chemical compounds. Knowledge of these values is of great importance for different fields of chemistry and physics. They have practical application in separation processes, studies of solubility of substances and their distribution in environment. Vaporization/sublimation enthalpies also play an essential role in the analysis of intermolecular interactions in condensed phase. Numerous experimental techniques have been developed for determination of phase transitions enthalpies. Generally, conventional techniques can be divided into two groups: calorimetric techniques, in which the phase change enthalpy is measured directly, and techniques in which vapor pressure is measured directly or indirectly as a function of temperature. Also, some methods based on gas chromatography were developed to measure vaporization enthalpies. All these methods were applied for many years by different groups of authors for the determination of vaporization/sublimation enthalpies of different series of compounds. The last compilation of vaporization/sublimation enthalpies was published by Acree and Chickos [1]. This database contains thousands of thermochemical values measured during the last two centuries. The analysis of this database shows, that despite the great amount of literature data for some compounds enthalpies of phase transitions are absent or in disarray, especially for large branched organic molecules, which are very often thermally unstable.

It is generally accepted that currently used methods for determination of the enthalpies of vaporization and sublimation are not universal. Their advantages and disadvantages are well documented in the literature [2]. Basically, conventional methods examine the transition of studied substances from a condensed phase to a gas phase at elevated temperatures. In this regard, the researchers who use these methods have problems with the study of low volatile and thermally unstable chemical compounds. Heat capacity difference between two equilibrium phases of a studied compound (solid and gaseous phases in case of sublimation, liquid and gaseous phases in case of vaporization) must be known in order to adjust experimental values by Kirchhoff's equation to the reference temperature which is usually 298.15 K. While the heat capacity in condensed phase can be measured experimentally,

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http://dx.doi.org/10.1016/j.jct.2015.07.037
0021-9614/